

THE PROGRESS

OF

HELIOCHROMY;

OR,

PAINTING IN COLOURS BY LIGHT.

COMPILED BY

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## HELIOCHROMY, &c.

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THE object in compiling the following pages is to bring into notice the various papers which have been scattered amongst numerous publications, and it is confidently believed they will be useful to those persons who wish to cultivate this branch of experimental philosophy, which no one will deny is the most interesting of all the processes in Photography. It has been named Heliochromy, or the production of pictures in all their various colours by light; and although this mystery of nature has been discovered to a certain extent only, yet, by considering carefully what has been accomplished, it may lead many to make experiments resulting in valuable improvements, and perhaps to much better processes. The pictures, which are produced by photography, may be termed perfect engravings; but the desideratum required is to produce perfect paintings.

That this is not impossible, any one may be convinced by laying a piece of glass, painted with various colours, on positive paper, prepared with ammonia nitrate of silver; and by allowing it to print in sunshine for ten minutes or so, each different colour will be found impressed upon it—the blue and the red very decided indeed.

But the most successful substance capable of producing all the colours, is a combination of pure silver with chlorine, producing a subchloride, as in M. Becquerel and M. Niepce's processes, the first with hydrochloric acid and the galvanic current, the other with solutions of the chlorides of iron and of copper, with or without the galvanic current,

as well as numerous other chlorides, in all cases applied to the well polished daguerreotype plate; but these are by no means the only compounds by which all the colours, or many of them, have been produced; the juice of flowers, the bromo-iodized plates, gum guaiacum combined with chlorine, and others, may be mentioned. It is true all attempts to fix what has been done by this means has hitherto failed; yet it can hardly be doubted but this will come in good time. The first thing unquestionably is to perfect the process; and certainly none have done more towards this than MM. Becquerel and Niepce of Paris; although it is right to mention that Sir John Herschel and Professor Hunt<sup>1</sup> succeeded in getting the colours of the spectrum (although by a different method), long before the illustrious Frenchmen made their processes known. Now the perfecting of the process lies in the accelerating of it. The length of exposure necessary in the camera at the present is far too long to be of any practical use. It will certainly install the individual high in the history of this science, who is fortunate enough to discover the means of making it as quick in action as the daguerreotype now is; when this is done, there will unquestionably be as great a difference in value between a good heliochrome and a daguerreotype as we have now between the best painting and engraving, so much would the one surpass the other. We would therefore press on those who take an interest in the new art to devote a portion of their time to experiments towards this end, and hope that they will be liberally rewarded for their labours in the fortunate discovery of some accelerating and fixing agent, and thereby perfect M. Niepce's already beautiful process. The papers of Mr James Campbell, Dayton, America, will abundantly shew that he has not laboured in vain, having brought to light many new facts, and suggested many va-

<sup>1</sup> It is a curious fact, very creditable to Professor Hunt, that scarcely a substance has been found to improve photography in general, but what has been previously mentioned by him in some of his works.

valuable experiments. He writes to the editor for Humphrey's Journal:<sup>1</sup> "I agree perfectly with your correspondent, that we are on the threshold of nature's laws, and that there need be no jealousy, for there is enough for all to do. If all would, like him, devote a part of their time to experiments, we might reasonably hope that many new discoveries would be added to photographic science. As to myself, I probably have as little time for experiment as any of your readers, yet I devote all my leisure time to it from pure love of scientific research. I was only induced to publish the results of my experiments by the hope of stimulating others to the like, and perhaps to more successful investigations.

"With this view, I have published, and intend to publish, the result of experiments which are only partially successful, believing that a knowledge of them may serve in some degree for data, and save much time and trouble to those engaged in like investigations. We have every reason to congratulate ourselves on the comparatively rapid development of natural colours in heliography, as it is only about four years since, that an eminent philosopher, one of the first standing in the scientific world, declared that 'it was utterly visionary ever to expect to produce natural colours, by any photographic process;' and scientific men generally appeared to agree with him.

"The experiments of M. Becquerel, however, soon shewed the fallacy of the conclusion, and opened a new field for scientific investigation.

"The researches of M. Niepce have thrown much light upon the subject, and they are especially valuable for the clear theory which they furnish on the production of the different colours on the metallic plate. The only well-authenticated experiments which have been in any degree successful in copying the colours of the prismatic spectrum on paper, are those of Hunt and Herschel, the former having

<sup>1</sup> Humphrey's Journal.



succeeded in producing more or less perfect copies of the prismatic spectrum with the salts of silver, and the latter with the colouring matter of flowers. (See Hunt's excellent work on Photography). The researches of these gentlemen, although of no direct practical value, are, however, invaluable to the experimenter, and exceedingly interesting. I have sometimes obtained an impression of the coloured spectrum on the chloride of silver on waved or oiled paper ; but the experiment is by no means certain, and I have never yet succeeded in copying a coloured engraving on it. I believe it, however, to be practicable.

"It is well known that Daguerre spent more than nine years in his experiments before he thought of exposing the iodized plate to the vapour of mercury ; and it is probable that some substance may yet be found equally efficacious, in the development and fination of coloured photographs. When this one thing is discovered, there will be little else to desire, and some lucky operator may, by some fortunate experiment, revolutionize the whole system of photography. Heliochromy will then supersede all other photographic processes whatever.

"I will now merely say that I hope our operators will experiment and publish every thing which has a practical bearing on the subject. We may then hope for an early solution of this interesting problem."

To those who have spare time, the repeating of the experiments of M. Niepce would prove very pleasant, and at the sametime interesting and useful. They are capable of very varied modifications, owing to the substances mentioned in his papers being distinct and numerous ; and it is known that the smallest deviation, in any of the operations of the daguerreotype process, gives a different character to the final result : and since even the addition of a little bromine vapour to the iodised plate accelerates the process a hundred-fold, may we not also expect that some slight modification in one or other of the known processes in he-

liochromy to produce like results? The encouragement given in the published accounts is clear to all who have carefully studied them, and those commencing experiments will not at all be at a loss for material, which, by combining, and varying, and adding to, in many ways, the numerous facts mentioned in these pages, will form a series of experiments of the most delightful description.

Sir John Herschel<sup>1</sup> was the first to obtain any good specimens of photographically impressed prismatic colourations. He exposed a paper prepared with a solution of guaiacum in spirit of wine to the action of chlorine considerably diluted with common air, by which it acquired a greenish-yellow hue. Transferred immediately to the spectrum, it was impressed with faint tints, nearly corresponding to the natural ones. The red was evident—the yellow dilute, and nearly white—the blue a fine sky-blue, while beyond the violet succeeded a train of somewhat greenish darkness. Professor Hunt<sup>2</sup> has in many instances got coloured pictures of the spectrum dark upon a light ground; but the most beautiful he has yet obtained has been upon the daguerreotype iodidated tablets, on which the colours have, at the same time, had a peculiar softness and brilliancy.

Daguerre himself has remarked that, when copying any red brick or painted building, the photograph assumed a tint of that character.

Professor Hunt prepared some papers with the bichromate of potass, and a very weak solution of nitrate of silver, which gave a blue, a green, and a red, under the respective colours.

He describes one of the most decided cases of colouration in his earliest researches. A paper was washed first with nitrate of silver, and then with the fluuate of soda. Under the spectrum the action commenced at the centre of the yellow ray, and rapidly proceeded upwards, arriving at its maximum in the blue ray. To the end of the indigo the

<sup>1</sup> Hunt's Researches on Light.

<sup>2</sup> Hunt's Photography, p. 150.



action was pretty uniform; it then appeared to be very suddenly checked, and a brown tint was produced under the violet rays, all action ceasing a few lines beyond the luminous spectrum. Some faint indications of change were evident to the lowest edge of the yellow, but none whatever below that point. The colours of this spectrum are not a little remarkable. I have now before me a spectrum impressed two months since, and the colours are still beautifully clear and distinct; the paper is slightly browned by diffused light, upon which appears the following order of colours:—A yellow line distinctly marks the space occupied by the yellow ray, and a green band the space of the green; through the blue and indigo region the colour is an intense blue, and over the violet a ruddy brown.

Mr Fox Talbot observed very early, in his researches in copying paintings on glass, slight colouration. "It is in these pictures only," says he, "that, as yet, I have observed indications of colour. . . . It would be a great thing if, by any means, we could accomplish the delineations of objects in their natural colours. I am not very sanguine respecting the possibility of this; yet, as I have just now remarked, it appears possible to obtain at least some indications of variety of tint."

Professor Hunt mentions,<sup>1</sup> in the summer of 1843, when engaged in some experiments on papers prepared according to the principles of Mr Fox Talbot's calotype: "I had placed in a camera obscura a paper, prepared with the bromide of silver and gallic acid. The camera embraced a picture of a clear blue sky, stucco-fronted houses, and a green field.

"The paper was unavoidably exposed for a longer period than was intended—about fifteen minutes; a very beautiful picture was impressed, which when held between the eye and the light, exhibited a curious order of colours. The sky was of a crimson hue, the houses of a slaty blue, and the green fields of a brick-red tint."

There is another very curious fact, pointed out in the first instance by Sir John Herschell,<sup>1</sup> with regard to bromide of silver, viz. that the red ray, the least refrangible, also produces a very considerable chemical action upon it.

This ray is red, and in nineteen cases out of twenty (it is not always the case, but in nineteen cases out of twenty) the impression which the red ray makes upon the bromide is of a red colour! And, in some cases, as will be found in Sir John Herschell's statement, it approaches even to the brilliancy of crimson.

In 1840, Professor Hunt<sup>2</sup> communicated to Sir J. Herschell the following curious results:—

“A paper prepared by washing with muriate of barytes and nitrate of silver, allowed to darken whilst wet in the sunshine, to a chocolate colour, was placed under a frame containing a red, a yellow, a green, and a blue glass. After a week's exposure to diffused light, it became red under the red glass, a dirty yellow under the yellow glass, a dark green under the green, and a light olive under the blue.”

The above paper, washed with a solution of iodine, is very sensitive to light, and gives a beautiful picture. A picture thus taken was placed beneath four flat bottles containing coloured fluids. In a few days, under the red glass and fluid, the picture became a dark blue, under the yellow a light blue, under the green it remained unchanged, whilst under the blue it became a rose-red, which in about three weeks changed into green. Many other experiments of a similar nature have been tried since that time with like results.

The *Comptes Rendus* of 12th February 1849, contains the report of M. Biot Chevreul and Regnault on M. Becquerel's memoir “On the Photo-Chromatic Image of the Solar Spectrum.” (The prospect, however remote at present, of being able to copy nature in all the truth of colour,

1 Journal of the Photographic Society, p. 73.

2 Researches on Light, p. 277.

gives great interest to every experiment which leads to an advance in this particular.)<sup>1</sup>

M. Edmund Becquerel, to whom this branch owes so much, has very recently succeeded in impressing upon a daguerreotype plate all the colours of the solar spectrum, and, to a certain extent, those of coloured drawings and natural bodies. Previous to this discovery, he had observed that red rays, which exercised almost no action upon sensitive paper prepared in the dark, acted much more rapidly upon the same paper after it had been exposed to light; and that, while the paper in the first of these states gave only a brown or slightly violet colour in the most refrangible rays, the paper in the second state, or after exposure to light, gave variable colours, recalling those of the rays which produced them, and even developed these colours in the less refracted parts of the spectrum. Pursuing the subject, he was led to the method of preparing the plates for receiving coloured impressions. After polishing the plate with English rouge or Tripoli, he fixes it on a small support formed by two copper wires in the shape of a fork, which holds it by means of two hooks at its extremities. The two wires are joined at the upper end, which is put in communication with the positive pole of a pile composed of two elements of Bunsen's pile, of an average charge. The plate is then plunged into a large vessel, containing from 8 to 10 litres (14 to  $17\frac{1}{2}$  pints) of chlorohydric acid, diluted in the proportion of 125 cubic centimetres of common chlorohydric acid to 1 litre ( $1\frac{1}{2}$  pints) of water. Into the same vessel there is plunged a rod or narrow strip of platinum, which communicates with the negative pole, and this rod is moved rapidly backwards and forwards, parallel to the surface of the plate, and at a certain distance from it. The plate of silver takes successively the different colours of thin plates, which may be readily seen when the room is feebly illuminated. The colour commences with grey,



then come the yellow and violet tints: it then passes to bluish and greenish, and then a whitish grey; then rose-coloured, then violet, and lastly blue. The operation is stopped before this second blue tint appears, and then the plate has a lilac tint. It is then quickly taken from the bath, plunged in distilled water, dried by slightly inclining it, and heating it gently with a spirit lamp, and blowing upon its surface. The immersion of the plate continues only one or two minutes. Were it kept longer, its colour would become deeper and deeper, and finally black, in which case it would become less and less sensible to luminous radiations.

Plates thus prepared would keep for an indefinite time in the dark. Before using them, the surface should be well rubbed with a pledget of cotton, to make it brilliant. These plates take a grey tint in diffused light. When a pure and concentrated solar spectrum is thrown upon the plate, the orange and red rays first develope a red colour, which increases rapidly in intensity, but at the same time deepens and finally becomes black. The photogenic action of this spectrum is prolonged considerably beyond the ray A of Fraunhofer, producing an amaranth tint, or one passing from red to violet. The prismatic green is green on the plate, and the blue and the violet produce their own colours, which are very fine and very intense at a certain period of the action. The yellow and orange are impressed with difficulty, but still they are seen on the plate after the first moments of action. There is a distinct action beyond the violet and the lavender-grey band beyond H, and stretching much beyond this band. The tint is greyish, becoming very sensible after ten or fifteen minutes' exposure, and then growing deeper and deeper. This portion of the photogenic spectrum, viz. that beyond H, shews itself very clearly by breathing upon it. The vapour condenses itself then in preference, and under the form of small liquid globules.

If the prepared plate of silver is heated before exposing to the action of light, it acquires new properties; while light impresses upon it a positive image, which comes out, and sometimes makes the ground as white as paper. When the plate is heated in a stove at  $100^{\circ}$ , it assumes, after a few minutes, a slightly reddish tint, which is the state most suitable for receiving all the colours of the spectrum. In this state the solar spectrum impresses upon it all its colours. The yellow and the green are very fine, the blue and violet take bright and clear colours, and the orange and the red have a great intensity, but their shades are more violet than those of the spectrum.

Beyond the red the effect is scarcely sensible, and beyond the violet there is a grey band, which grows deeper and deeper. When the solar spectrum is very concentrated, a fine coloured impression of it is obtained in a few minutes; but when it is dilated, and produced from a narrow aperture, one or two hours are required, and in this case the principal black lines of Fraunhofer are produced in black.

M. Edmund Becquerel has also produced upon his plates copies of coloured prints, but the colours are much fainter than those of the solar spectrum.

He has also obtained, by the camera obscura, pictures still more distinctly coloured of brightly coloured objects, but they require a long exposure in order to obtain pictures of a certain intensity.

These photo-chromatic pictures may be preserved a long time in the dark; but they become faint under the prolonged influence of diffused light, and M. E. Becquerel has tried in vain to fix them.

The Athenæum adds, "We may therefore reasonably hope, that eventually the pencil of the sunbeam will add the charm of colour to the chemical pictures which it produces."

According to the preparation of the plate and the thick-



ness of the sensitive coating, any of the tints of the spectrum may be made to predominate.<sup>1</sup> Thus, a surface well prepared, and previously in diffused light-coloured purple under a deep red glass, gives a beautiful coloured photographic image of the spectrum, in which the orange-yellow, the green, and the blue, are marked with the greatest clearness. The substance formed upon the surface of the silver is not the white chloride, but probably a subchloride, since it is not strongly coloured beyond the visible violet, as the chemically precipitated chloride is, and the maximum of action is found in the yellow, where the maximum of luminous intensity is, or moves towards the red according to the preparation of the plate. To get a tolerably rapid action, it is necessary to use a strongly concentrated spectrum. These effects explain the red colour of the chloride of silver, and of the sensitive paper formed with that compound, in the red rays, which has been already observed by MM. Seebeck and Herschel.

M. E. Becquerel has succeeded in preparing, by means of free chlorine, and also by using bichloride of copper, a sensitive coating of the chloride of silver, so impressed that now only certain parts of the spectrum are represented with their colours; but, besides, white light makes a white impression.

When the action of the spectrum is permitted to last a long time, the tints become dark, and the image finally takes the metallic lustre: the colours have then disappeared. If the fixation could be accomplished, and if the sensitiveness of the material was greater, we could not only draw but also paint by light. Nevertheless, the results mentioned shew that the solution of the problem is possible.

The next and most important process in the art is that of M. Niepce de Saint Victor,<sup>2</sup> a translation of which is

<sup>1</sup> Year Book of Facts.

<sup>2</sup> *Comptes Rendus*, June 2, 1851.

given in the *Chemist* of August 1851. As it is the most useful, we give it in full.<sup>1</sup>

“ I deposited at the Academy of Sciences, on the 24th of March last, a very detailed memoir on this subject, of which I now give as succinct an analysis as possible.

“ It is known that a plate of silver immersed in a solution of sulphate of copper and chloride of sodium, at the same time rendered electro-magnetic by means of a battery, is chloridised, and becomes susceptible of receiving colour when, on being withdrawn from the solution, it is exposed to the action of the light.

“ It is also well known that M. E. Becquerel, by exposing this plate to the coloured rays of the solar spectrum, obtained an image of this spectrum in such a manner that the red ray produced on the plate an image of a red colour, the violet ray a violet colour, and the same with the other rays. My observations having led me to think that it was possible there might be some relation between the colour which a body communicates to a flame, and the colour which light developes on a plate of silver which had been chloridised with the body which colours that flame, I undertook the series of experiments which I now submit to the Academy.

“ The bath in which I immersed the plate of silver was formed of water, saturated with chlorine, to which I added a chloride endowed with the property of colouring flame with the colour which I wished to reproduce on the plate.

“ For example, it is well known that chloride of strontium gives a purple colour to flames in general and in particular to that of alcohol.

“ If a plate of silver be prepared by passing it through water saturated with chlorine, to which chloride of strontium has been added, and if afterwards the back of a drawing containing red and other colours be applied against the plate, and the whole exposed to the light of the sun for ten or fifteen minutes, it will be found that the colours of the

<sup>1</sup> Extract of a Memoir on a relation existing between the colour of certain coloured flames with the Heliographic images coloured by light. By M. Niepce de Saint Victor.

picture are reproduced on the plate, but that the red is much more distinct than the other colours.

“When we wish to reproduce successively the other six rays of the solar spectrum, the same method must be employed as that followed in the case of the red ray, by employing the chlorides of calcium and uranium for orange, hypochlorite of soda, or the chlorides of sodium or potassium, as also pure solution of chlorine, for yellow ; for if we steep a plate of pure silver in a solution of chlorine for some time, and if we afterwards expose it to the flame of a spirit-lamp, a beautiful yellow flame is produced.

“When a silver plate is immersed in a solution of chlorine, or when the plate is exposed to its vapour (but in the latter case the plate always remains dull, although the colours are reproduced), all the colours are obtained by the light, but the yellow is the only one that is at all vivid.

“I have obtained very beautiful yellows with a bath composed of water, slightly acidulated with hydrochloric acid, and a salt of copper. The green ray was obtained by means of boracic acid and chloride of nickel, as well as all the salts of copper.

“The blue ray is obtained by the employment of the double chloride of copper and ammonia. The indigo ray is obtained with the use of the same substance ; the violet ray with chloride of strontium, and sulphate of copper.

“Lastly, if alcohol acidulated by hydrochloric acid be inflamed, a yellow, blue, and greenish flame is obtained ; and if the plate of silver be prepared with water acidulated with hydrochloric acid, all the colours are obtained by the action of light ; but the ground of the plate is always black, and this preparation of the plate can be made only by means of the battery.

“These are all the substances producing coloured flames, which also furnish coloured images by means of light. I find that substances which do not produce coloured flames, do not give coloured images by light ; that is to say, only



a negative image is produced on the plate, composed only of black and white, as in ordinary photography.

"Some substances give white flames, such as chloride of antimony, chlorate of lead, and chloride of zinc. The first two give a bluish white flame, and the last a white flame with a greenish or bluish tint. These three chlorides give no colour with light if employed alone ; but if they are mixed with other substances which produce colours, we obtain, in addition, white grounds, a very difficult thing, because, from the fact that there does not exist either black or white, properly so called, in these phenomena of colourations ; and if I have been able to obtain them, it is only by means of the chloride of zinc or chlorate of lead which I added to my baths, but in very small quantity, because they prevent the reproduction of colours. I have reproduced all the colours of the model by preparing the plate with a bath composed of deutochloride of copper.

"This result is easily explained. It appears to me by the observation that a flame of alcohol or wood, to which chloride of copper has been added, presents not only green, but also successively all the other colours of the spectrum, according to the intensity of the fire. It is the same with almost all the salts of copper mixed with chlorine.

"I will now refer to the supplement of my memoir, which will be found entire at the conclusion of this extract, and in which I have placed in categories all the substances which, in the state of chlorides or chlorates, have an action in these phenomena of colouration. The substances which do not give coloured flames, do not give coloured images with light.

"I give in my memoir the composition of the baths with which the silver plate is prepared ; but as they are numerous, and as, moreover, I have not noticed all the combinations I have made, I have selected two or three of them which have appeared to me preferable, especially for preparing the plate without making use of the battery. I have

already stated, that liquid chlorine impressed the silver plate by a simple immersion, and gave all the colours; but they are feeble, with the exception of the yellow. This is because the layer is too thin, and it can be made thick only by means of the battery. If we put a salt of copper into liquid chlorine, a very thick layer will be obtained by simple immersion; but the mixture of copper and liquid chlorine is always badly made. I prefer taking deutochloride of copper, to which I add three-fourths of its weight of water. This bath gives very good results; however, I prefer a mixture of equal parts of chloride of copper and chloride of iron, with three-fourths of water. The chloride of iron has, like that of copper, the property of impressing the silver plate, and of producing several colours; but they are infinitely weaker, and the yellow always predominates. This accords with the yellow colour of the flame produced by the chloride of iron.

“If a bath be formed composed of all the substances which, taken separately, give a dominant colour, very vivid colours will be obtained; but the great difficulty is to mix them in suitable proportions, as it almost always happens that some colours are excluded by others.

“I must not omit to mention, that there exists great difficulty in obtaining the colours, still more so than in all other photographic processes; for although the plates may be prepared in the same manner, the same results are not always obtained. This arises, amongst other causes, from the thickness of the coating of chlorine, and its degree of concentration, which varies according to the chlorides employed.

*“On the Influence of Water and Heat in these Phenomena of Colouring by Light.*

“The influence of water is indubitable, as dry chlorine produces no effect; whilst by the employment of chlorine rendered liquid by immersion, or by aqueous vapour, the re-



production of all the colours which I have named are obtained. With regard to heat, I have noticed that when the plate, which has been submitted to the action of chlorine, is heated from underneath by the flame of a spirit lamp, it takes successively all the colours produced by heat.

“Thus the plate when taken from the bath is of a dull colour, takes successively by means of heat the following colours, viz. reddish brown, cherry red, bright red, up to a white tint. In this latter state it produces no effect when exposed to the light; the exposure should take place at a cherry red heat.

*“General Observations on these Phenomena.*

“It is a remarkable circumstance, that in order to obtain these colouring effects, it is absolutely necessary to operate on metallic silver, prepared as I have mentioned; for the nitrate, the chloride, the cyanide, and the sulphate of silver, spread on paper or starch coating, give only black and white. It may perhaps be that by employing silver in powder, mixed with the substances which I have named, some result may be obtained by coating a sheet of paper with the mixture;—this is an experiment which I intend to make. I have already tried silvered paper with good results, but not so satisfactory as those furnished by the metallic plate. We have seen that all the substances which give coloured flames, give also coloured images, and almost always in relation with their respective colours. For if I have not been able to isolate completely a ray, that is to say, to obtain but one single colour on the plate, to the exclusion of all others, I have always obtained a dominant colour according to the substance which I have employed; and if we cannot obtain a single colour, it is because the chlorine, which is the indispensable substance for obtaining them, produces them all by itself, as we have seen in operating with pure liquid chlorine; but in this case the colours are always very feeble, whilst they separately

assume much vivacity, according to the substances which have been employed in mixture with the liquid chlorine.

“Neither iodine nor bromine can be employed like chlorine for this purpose. Neither of them produce colours or coloured flames : Even when they are combined with copper they give only a green flame. Chlorine, in the state of chloride or chlorate, is the only substance which gives to metallic silver the property of being coloured by light. I have also observed that certain colours took a longer time to appear, and that during this time others had disappeared.

*“Mode of Operating.*

“All my baths or solutions were formed in the proportion of one-fourth by weight of chloride, and three-fourths of water. These are the proportions which I have found to be most suitable. When hydrochloric acid, with a salt of copper, is employed, it must be diluted with one-tenth its weight of water. The liquid chlorine must not be in too concentrated a state if fine yellow colours are required.

“In baths composed of several substances, it is essential to filter or to decant off the liquor, in order to obtain it very clear ; it is then kept in a jar ready for use as occasion may require.

“More of this solution must not be taken than will be necessary to prepare two plates at the most, because the bath becomes considerably weakened at each operation ; it may, however, be revived by the addition of a few drops of hydrochloric acid.

“When operating on silver of a standard of 1000th (pure silver), I have obtained colours more lively than on a plate which contained one-tenth of copper. I then operated on a silver plate of the standard  $\frac{718}{1000}$ , when I obtained only very dull colours ; hence it is preferable that the silver should always be of the purest quality for these experiments.

“The plate being completely polished (for which

tripoli and ammonia must be employed), it is immersed in the bath at one stroke, and allowed to remain there for some minutes, in order to receive a coating of sufficient thickness. On removing the plate from the bath, it must be rinsed in a large quantity of water, and then dried over a spirit lamp. In the bath it assumes a dull, almost black colour; and if thus exposed to the light, the colours are equally produced, but much more slowly, and the ground will always be black. In order, therefore, to obtain a clear ground, and that the operation may be more rapid, the plate must be brought by heat to a cherry colour; and it is at this point, as I before said, that it should be exposed to the light. The length of exposure varies very much, according to the preparation of the plate; but it may be calculated that two or three hours will be required to obtain a proof in the camera. This is certainly a long time; but the question of accelerating the operation being but a secondary one, I have not as yet turned my attention to it. I may, however, mention that fluoride of sodium, as well also as chloric acid, and all the chlorates, much accelerate the operation.

*“On fixing the Proofs.”*

“Hitherto I have not been able to fix the colours; they disappear very quickly; even in diffused light there is no preserving them. I have made more than a hundred attempts, but without obtaining the least satisfactory result. I have tried all the acids and all the alkalies; the former freshen up the colours and the latter take them out; destroying the chlorine, and leaving only a dark image. It is by this means that I have obtained proofs identical with the daguerreotype image, and sometimes without any of that mirror-like appearance common to them. It is sufficient, in order to obtain the last, to have a very thick layer on the plate, and not to leave them exposed to the light so long.

“The problem of fixing the colours still appears to be very



difficult of solution; nevertheless I still continue my researches, and have already succeeded in a momentary fixation of them, by exposure of the colours to the flame of a spirit-lamp containing chloride of sodium and hydrochlorate of ammonia.

"I have ascertained that these phenomena of colouring are exhibited as well in vacuo as on exposure to the air; consequently oxygen performs no part in the operation. The three agents are water, heat, and light, which is the principal. I have studied the property of each chloride, both separately and simultaneously with liquid chlorine, or with a salt of copper; for if the plate be not prepared by means of the battery, a salt of copper is indispensable for obtaining a layer of a certain thickness, and in this case the colours are less vivid.

*"Supplement to the Memoir presented to the Academy on the 24th March 1851.*

"I have proved that these phenomena of colouration by light are manifested in vacuo, as well as in the air, consequently oxygen performs no part. There remain, therefore, three agents—water, heat, and light—the last being the principal one.

"I now give the nomenclature of all the chlorides which I have employed, arranged categorically.

*"Action and Properties of each Chloride.*

*"First Category.*—Chlorides which, being employed alone, act on the silver plate in such a manner as to make it take all or many of the colours of the model.

"These are the chlorides of copper, iron, nickel, and potassium, and the hypochlorites of soda and lime, as well as liquid chlorine by immersion or in vapour.

*"Second Category.*—Chlorides which, employed alone, act on the silver plate, but which do not give coloured images with light. These are the chlorides of arsenic, antimony, bromine, bismuth, iodine, gold, platinum, and sulphur.

*“ Third Category.*—Chlorides which, employed alone, do not act on the silver plate, but which act on it when mixed with a salt of copper (especially with sulphate or nitrate of copper), and which then give colours with the aid of light. These are the chlorides of aluminum, silver, barium, cadmium, calcium, cobalt, tin, manganese, magnesium, phosphorus, sodium, strontium, and zinc.

“Hydrochloric acid, diluted with one-tenth of its weight of water, and mixed with nitrate of copper, acts on the plate, and gives all the colours.

*“ Fourth Category.*—Chlorides or chlorates which, although mixed with a salt of copper, and acting on the plate of silver, do not give colours by light; these are chloride of mercury and chlorate of lead. To sum up; the first category contains the chlorides which, being employed alone, act on the silver plate in such a way as to make it take all or many colours, and, which is a remarkable thing, all these chlorides likewise give, by combustion, coloured flames.

“The second category contains chlorides which act on the plate when employed alone; but as none of them give coloured flames, so they do not give coloured images by light, even when mixed with a salt of copper.

“The third category contains the chlorides which alone do not act on the silver plate, and which do not give coloured flames (with the exception of those of barium and zinc, which give feeble colours), but by mixing them with a salt of copper, chloride of copper is formed, and they become, in this case, capable of acting on the plate, and of producing colours by light.

“The fourth category contains the chlorides which, although mixed with a salt of copper, and in this case acting on the silver plate, do not produce colour with light. They do not either give coloured flames when burned alone and combined with a salt of copper; they give only a green flame.

“There exist also a great number of chlorides, on which



I have not experimented, because they are too high in price to be employed, especially in forming baths.

"These chlorides are those of carbon, cerium, chromium, cyanogen, iridium, molybdenum, palladium, silicium, rhodium, titanium, tungsten, and zirconium.

*"Conclusion.*

"During the year that I have been occupied with these experiments, I have observed many facts. I have repeated the experiments a great number of times, and it was only after doing so that I wrote the memoir, which I have had the honour of presenting to the Academy.

"Now, according to the facts which I have observed, it appears that, if there is not a complete similarity between the coloured flames, and the coloured images obtained by light on a plate of silver prepared with the chlorides or chlorates which colour flames, there is a great analogy between these colours.

"Professor Hunt remarks<sup>1</sup> on the above process: 'At the same time the chloride of silver is formed, some subsalts of copper combine with this chloride, forming a compound which is of a chocolate brown colour. This picture is the result of different degrees of degradation, as it were, produced upon the plate by the combined influences of the chemical and of the luminous rays. The yellow ray of the prismatic spectrum possesses a greater degree of interfering action upon the chemical agency than any of the other rays; consequently, there is less chemical change under that portion on which yellow light falls than under the other, and then a yellow colour is the result.'

"When we go on towards the other end producing a deeper and deeper degradation, by chemical or physical change, we get the blues, the greens, and the violets. There are some peculiar principles involved in this change that we do not as yet understand. The whole of the pheno-

<sup>1</sup> Journal of the Photographic Society, p. 22.

mena are yet obscure, and require a most searching investigation. It appears the colours produced, howsoever obtained, must be the result of that balancing power between the luminous and the chemical agencies which is constantly taking place; and therefore we can perfectly understand that when the balance is in a certain condition, we may get the surface so far chemically changed, that it is in the physical state to send back yellow rays to the eye. Then the chemical principle being a little more active, and the luminous principle not so effective, red rays are the result; but when the chemical agent becomes still more active, the luminous principle being weaker in action, we get a blue radiation.

“In this new memoir, my principal observations are on the optical phenomena which have presented themselves in trying to fix the colours in the camera obscura.<sup>1</sup> After having obtained by contact (that is to say, by applying the right side of a coloured engraving on a sensitive plate, and covering with a glass, and exposing it afterwards to the light), a copy in all the colours, I have endeavoured to arrive at the same results in the camera. After encountering great difficulties, I find myself just at a certain point to surmount them.

“The production of all the colours is possible, but not without properly preparing the plate. I have begun by reproducing in the camera obscura coloured engravings, then artificial and natural flowers; and lastly, dead nature, a doll dressed in stuffs of different colours, and always trimmed with gold and silver lace. I have obtained all the colours; and what is still more extraordinary and more curious is, that the gold and silver are depicted with their metallic lustre, and that rock-crystal, alabaster, and porcelain, are represented with the lustre which is natural to them. In producing the image of precious stones and of glass, I observe a curious peculiarity. I have placed before a lens a deep green gem—an emerald, which has given

<sup>1</sup> La Lumière, No. 47, 13th November 1857.

a yellow image instead of a green one; whilst a clear green flint glass placed by the side of the other, is perfectly reproduced in colour.

"The greatest difficulty is that of obtaining many colours at the same time on the same plate; it is, however possible, and I have frequently obtained this result. I have observed, that bright colours are produced much more vividly, and much quicker than dark ones, that is to say, the nearer the colours approach to white, the more rapidly are they produced; and the more closely they approach to black, the greater is the difficulty in producing them. Of all others, the most difficult to be obtained is the deep green of leaves; the light green leaves are, however, reproduced very easily.

"To obtain the deep greens, the plate ought hardly to be heated before exposing it to the light, whilst to obtain most of the other colours, and, without doubt, the beautiful whites, the plate ought (as I said before) to be brought to the cherry red tint with its sensitive coating.

"This red tint has great inconveniences; the blacks and the shadows remain almost red at times; however, we get the blacks well indicated, and always when we operate by contact.

"If after taking out of the bath the plate is dried without elevating the temperature, only to a point which changes the colour, and exposed to the light, covered with a coloured engraving, we readily obtain, after a very short time, the engraving with all the colours; but very often the colours are not visible, some one only appearing; these are the greens, the reds, and sometimes the blues. The other colours, and frequently them all, though certainly produced, are resting in a latent state; for if we take a tuft of cotton with a little ammonia on it, having already been used to clean a plate, we see the image appear by little and little with all the colours—that must be done to raise up the upper coating of chloride of silver, to get to the under coating which adheres to the silver plate, and on which the



image is formed. We see by this that the business is to find a substance which will develop the image, and, as it ought at the same time to fix the colours, the problem will then be resolved entirely. If we employ the vapour of mercury, we develop the image very well ; but it is of a uniform grey tone, without any trace of colour ; its appearance differs from that of the daguerrean image in this, that it shews itself without two different aspects, that is, the positive image in one way and the negative in another.

“ If we employ a weak solution of gallic acid, with some drops of ammonia added, the image appears equally without doubt when heated a little, and when we afterwards dry the plate without washing, the image which appears then is like that produced by the mercury ; and if we throw into the gallic acid some drops of aceto-nitrate of silver, it ought to be almost black.

“ The time of exposure necessarily varies considerably. I have much abridged it, having made proofs in the sun with an English lens for half plates in less than a quarter of an hour, and in less than an hour in diffused light. The more the plate is sensitive, the more the colours pass quick ; and to this moment I have not fixed the colours, but only imperfectly. The question of fixing the colours is not yet resolved ; it is bound, it may be, as I have indicated above, in the discovery of a substance which will make the image pass from the latent to the visible state.

“ Although this rests to be done, I believe I have already obtained extraordinary results, which have surprised all those persons to whom I have shewn the proofs of my doll. Where the lace of gold and silver has been produced with their metallic lustre, the model of the figure and all the colours of the dress have been drawn with great clearness. The best proofs have already realized in part the enthusiastic hopes of my uncle, who said to one of his friends, the Marquis de Jouffray, that one day he would produce the image such as it is seen in a mirror.

“ Unhappily this great progress is not yet attained ; and although the difficulties are yet numerous and grave, I have put, I am sensible beyond a doubt, the possibility of a complete method.

“ I still reserve to myself the mode of preparing the plates by which I have made these results, and which I have the honour to dispose on the Bureau.

Nov. 6, 1852.

“ NIEPCE DE SAINT VICTOR.”

“ DAYTON, *January* 20, 1853.

“ As the subject of Heliochromy is now exciting considerable attention among artists, and those fond of scientific experiments, I have concluded that a short article on the subject might not be unacceptable to your readers.<sup>1</sup> I furnished a short article to the *Scientific American* a few weeks since, giving the results of experiments on the chloridated plate with iodine, bromine, fluorine, and chrome, either separately or in combination, to which those interested in the matter may refer.

“ It is well known that light produces little or no change on perfectly pure chloride of silver, but that the latter is rapidly blackened if organic matter be present, and that this organic matter is generally found in the water with which it has been washed, or in the solution from which it has been precipitated. When the chloridated plate is exposed to light, this organic matter is decomposed, oxygen being eliminated, and the free nascent hydrogen is employed in decomposing and reducing the chloride, and an opposite state of electrical excitement is induced. Now, MM. Becquerel and Niepce de St Victor have proved that, if chloride of silver containing a slight trace of copper be exposed to the prismatic spectrum, or to rays of different colours while undergoing this reduction, it is susceptible of colouration after a protracted exposure. From this it would seem that this process might be much accelerated if we were

<sup>1</sup> Humphrey's Journal, p. 333.

careful to aid nature in her operations, instead of trying mere hap-hazard experiments not founded on rational theory. I will show by a few experiments that this may be done, and to avoid being too prolix, will at present speak only of the chloridated silver plate unaccelerated by iodine, bromine, fluorine, chrome, or their compounds. If the plate covered with the enamelled chloride of silver, prepared by Niepce's process, be exposed to a current of hydrogen while receiving the image, the process will be much accelerated, and the image will be impressed in from half an hour to an hour, according to the quantity of gas passed into the camera, the light, temperature, and electric state of the atmosphere, &c. instead of requiring from three to five hours, as in the original process; and the colours of the picture will be impressed on the plate in all their original beauty. This experiment may be very easily performed, it only requiring a few grains of zinc in a small vial containing diluted sulphuric acid. The vial and its contents may be placed in the camera, and the hydrogen, being nascent, is in its most active state; and as it is perfectly transparent, it permits the light to act on the plate, while it is itself engaged in reducing the chloride, which it is capable of doing only in sunlight. The hydrogen, probably from its affinity for oxygen, hastens the decomposition of the organic matter, and assists in reducing the chloride, thus acting as a de-oxidating and dechloridating agent. There was, however, sufficient hydrogen contained in the combined organic matter to effect the reduction of the chloride; hence it is probable that the excess merely hastens the decomposition.

"Following this train of investigation, I have tried many other reducing agents, both liquid and gaseous.

"The most important liquid agents tried, have been the protosulphate and nitrate of iron, ferrocynade of potassium, protochloride of tin, and the fluorides of potassium and sodium. The principal gaseous agents tried are hydrogen



—alone, and in combination with carbon and sulphur—ammonia, sulphuric ether, in vapour, chloroform vapour, sulphuret of carbon, chloride of sulphur, hydrosulphuret of ammonia and sulphurous acid. As very remarkable results followed from the application of the gases, I will speak of them more particularly. Sulphurous acid has a strong tendency to abstract oxygen from organic bodies; it also unites with chlorine in sunlight, and so do light and heavy carburetted hydrogen; the latter indeed without the influence of light. Sulphurous acid abstracts oxygen from organic bodies with which it combines, forming sulphuric acid; and sulphuric acid renders chloride of silver unchangeable to light, by destroying the organic matter with which it is combined.

“I hence inferred that it might be used for the double purpose of reducing and fixing the picture.

“That it is a powerful accelerator is certain; the fixing requires further experiment. Pictures may be obtained with this gas in half an hour, by passing it, nascent, and in sufficient quantity, into the camera, and the colours are preserved. There is, however, a little sulphur sometimes deposited under the enamel, which gives the light parts of the picture a yellowish cast. This colour may sometimes be removed by heating the plate. Carburetted hydrogen acts still more quickly, probably from the free carbon which results from its decomposition, being a powerful reducing agent, and as the carbon is not left under the enamel, it probably passes off, under the form of the volatile chloride of carbon. I obtained one picture in five minutes, by passing into the camera the gases generated from the distilling alcohol and sulphuric acid in a retort. The gases formed were olefiant gas and sulphurous acid, mixed with a little light carburetted hydrogen and sulphuric ether. The colours were very fairly represented, but not so good as I had previously obtained. I consider this experiment as very encouraging; but having lately

tried it, have not repeated it by itself, without the agency of electricity. As electricity is a powerful agent in decomposing chemical compounds, it might be naturally inferred that it would aid in the process. I have often tried it, but until lately, without any very important results.

“Dry chloride of silver is not decomposed by electricity, yet it is decomposed by light, and other agents may by it be much accelerated; and I did not at first use a sufficiently powerful current. I now render the plate a part of the conducting medium which terminates at the positive pole, and terminate the poles in water, to which some saline constituent has been added, and by the decomposition of the water am enabled to judge of the power of the current. By using the gases at the same time that the plate is thus excited, I have been enabled to take pictures in from four to five minutes, which would otherwise require from three to five hours for their production. These pictures are developed under a hard, tough enamel of chloride of silver, cannot be rubbed out by the fingers, and will even bear considerable buffing; and if the enamel is thick, are improved by the operation.

“I have not been able to fix the picture permanently, but it will keep a long time, if not exposed too often and too long to the light. From the experiments, it seems that a prolonged exposure is not necessary to produce colouration; hence, agents of great energy may be employed in reducing the chloride.

“That colouration be produced, it is important; I think that the picture, by whatever process it is taken, be positive, and complete on its removal from the camera. For fixing, it is important that all the organic matter be destroyed, and then, I believe, it will be fixed. I am engaged at present in experimenting with iodine, bromine, fluorine, sulphur, chrome, and copper, and their compounds, deposited on the silver plate by electric action or otherwise, but have not as yet any results sufficiently matured to

publish; although I have produced colouration. Great care is requisite in preparing the enamelled plate of chloride, and some experience is required to judge at what state of its preparation it is most sensitive to light; yet any artist after a few experiments can prepare it. Having been obliged to make the greater part of the chemicals used, I have as yet been able to make but a very meagre investigation of this interesting subject.

“ J. CAMPBELL.”

“ As you have requested me to contribute a few articles to your Journal, I have, after mature deliberation, concluded to do so, but shall bespeak the favourable indulgence of your readers.

“ I feel that by many a great deal is expected from one who has announced any new discoveries in science; while they themselves remain quiescent until something of practical importance is produced, when they become all at once surprisingly active in appropriating to themselves any practical benefit which may be derived from it.

“ Others, however, are constantly on the watch for improvement, and are ever endeavouring, by well directed experiment, to contribute something to the advancement of their profession. It is to the latter class that I direct whatever of experiment or suggestion I may hereafter write, and shall be happy if by either I contribute in hastening the progress of science.

“ Indeed, where the field is so large, active intelligent experimenters are wanted; and while men so distinguished in science as Becquerel, St Victor, Herschel, Hunt, and Talbot, are actively engaged in investigating heliographic science, why can they not have active and intelligent co-operators on this side of the Atlantic? Here we have indeed Dr Draper, who has a place in the history of the daguerreotype only second to Daguerre himself; and numerous others, who have contributed more or less to the present high excellence in the daguerrean art.



“Why are they not actively engaged in investigating Heliochromy, and hastening the time, which will assuredly come, when pictures may be taken in natural colours, which shall be permanently impressed on the plate, and when, as the elder Niepce predicted, one may see himself represented as faithfully on the plate as in a mirror? That this result is certain I do not doubt; who will be able to do it no one can predict.

“It is well known that M. Becquerel first succeeded in transferring the coloured image, with certainty, to the metallic plate; but it is to M. Niepce de St Victor, that we owe the first clear theory of the production of these pictures, viz. that the chlorides of the different metallic and earthy bases communicate to the chloridated silver plate the property of being impressed by light, with the same colour which the body itself communicates to flame. M. Niepce was also the first to produce exact copies of coloured lithographs, and of nature itself, and his discoveries have won for him imperishable renown. I do not know whether most to admire M. Niepce's discoveries, or the generosity with which he has given to the world the details of a process which he was conscious of being able to perfect himself.

“Indeed, from M. Niepce's known character, there is no doubt that he would gladly hail any discovery which will contribute to the perfection of his process. Hence I cheerfully add my mite to the common cause, and in future will give some experiments on his process, and make some suggestions on other courses of investigation, which I believe from reasoning and experiment to be profitable, but which my limited time and means have not allowed me fully to investigate. I will add to the above a few practical remarks, which are in part suggested by the perusal of M. Niepce's last communication to the French Academy of Sciences.

“M. Niepce speaks of a possible development of the pic-

ture by some agent yet to be discovered, and speaks of ammonia as an agent with which he has been partially successful in fixing the colours. By reference to my first communication in the *Scientific American*, it will be seen that I spoke of rendering the picture very distinct in some cases, by reducing the thickness of the coating with an alkaline solution, and of a partial development of one picture with the sulphate of sodium.

"I used ammonia also, but had not remarked the fixation of the colours, and am not yet prepared, by experiment, to speak with certainty on the subject. Whoever attempts to fix the picture by ammonia must use it carefully, and in small quantity, or it will take both enamel and picture from the plate. Chloride of silver is very soluble in ammonia, and I generally use it to clean the plate.

"I have tried its vapour, but cannot speak of it with certainty, as I have tried it very recently.

"I think that to produce coloured pictures, they should be positive and complete on their removal from the camera; yet I have occasionally produced results which would seem to warrant a different opinion. In reducing the thickness of the enamel by alkaline solutions to produce greater distinctness, the operation is mechanical, and buffing will produce the same effect. But I have met with results, as to the mechanical or chemical nature of which I could not certainly determine. For instance, I once brought out a picture on the plate, when, after exposure in the camera, none at all was visible on it, by the aid of hydrogen, and succeeded in part at other times.

"I am at a loss to determine whether the development was produced by the diminished thickness of the enamel, or whether it was partly owing to a continuation of the action produced by the chemical rays. Hydrogen and chlorine mixed remain quiescent in the dark, or in ordinary diffused light; but if the mixture be exposed to the direct rays of the sun, it explodes with great energy. It will also ex-

plode if the chlorine has been previously exposed to sunlight, or if the electric spark be passed through the mixture.

“ If the action be caused by light, then it may truly be considered as a developing agent. For a fixing agent we want one which will destroy the organic matter, and yet not attack the reduced chloride or metallic silver which is developed under the enamel. In my next I will point out some courses of investigation which I believe worthy of experiment.

“ JAS. CAMPBELL.”

“ The process of M. Niepce is the only one known at the present time, by which we are enabled to obtain exact copies of natural objects ; and it is on that account worthy of our closest attention. When this process is sufficiently improved to enable us to take permanent impressions in the same time, and with the same light by which ordinary daguerreotypes are taken, it will be perfect.

“ Much, very much, however remains to be discovered before we can attain so desirable a result. Every artist should make himself acquainted with M. Niepce's process, and endeavour by careful experiment to improve on it. If every one would do so, we might reasonably hope that it would soon be perfected. The manipulations necessary for the preparation of the plate are but little more difficult than for the iodised plate, and they will form the subject of a future article.

“ I am, however, inclined to believe that colouration may be produced by other agents than the chloride of silver, and which may perhaps be more rapidly impressed, and less difficult to fix. The experiments of Herschel and Hunt have proved conclusively that colouration, as far as impressing the prismatic spectrum, may be performed by other agents. Mr Talbot's experiments on the iodised copper plate are also worthy of attention. Herschel's experiments on the colouring matter of flowers, and on the cyanotype, and Hunt's experiments on the bromo-fluoride of silver, are



"Herschel first noticed that paper, impregnated with the chloride of silver, when exposed to the prismatic spectrum, was impressed with tints which were nearly complimentary to the colours of the prismatic rays; and this fact may have suggested M. Becquerel's experiments on the chloridated plate.

"The chloridated plate is impressed with all the colours by light, but not certainly—one or the other colour predominating, according to the amount of chlorine in the liquid used in preparing the plate; and to obtain coloured impressions with certainty, a salt of copper must be employed. Hence the relations of copper to light become very interesting.

"If a plate of copper be raised to a red heat, and allowed to cool slowly while exposed to light, it will pass through all the colours of the spectrum, and at last become the black oxide of copper. Copper has also a red sub-oxide of exceeding beauty, which is used in staining glass, and the salts of the metal generally give a variegated flame before the blowpipe. These properties of copper render it the most important colourific agent in M. Niepce's process. If the silver plate be exposed to a current of dry chlorine, the chloride so formed is not any more susceptible of colouration than the iodised plate. To render the chloridated plate capable of colouration, it must be coated with the galvanic battery, the plate itself being immersed in a solution of some soluble chloride, which is decomposed by the current. It would seem then that if the iodised or bromidised plates were prepared in the same way, they would be more likely to receive coloured impressions.

"M. Niepce, however, says that he has tried unsuccessfully iodine and bromine, and their salts, by which term the iodides and bromides of copper are of course included.

"This is undoubtedly true as to the bodies above mentioned, as they always invariably produce negative pictures, and the application of any chemical to render them positive

would destroy any traces of colouration with which they might have been impressed. As the fluoride of silver is soluble in water, it is impracticable to produce a coating of fluoride by the decomposition of some soluble fluoride by the galvanic current.

“ We must then, if we wish to produce colouration, endeavour to render the pictures positive in all their stages.

“ The difficulties in regard to the reception of colouration by the ordinary agents used in taking photographic impressions, are admirably expressed by M. Biot.

“ The pictures taken on the chloride of silver are positive in every stage of their development. The enamelled chloride on which the pictures are taken is of a homogeneous non-crystalline nature, translucent, and somewhat resembling stained glass ; and the pictures are probably produced by the crystallization of metallic silver, or of the nearly reduced sub-chloride under the enamel. Iodine will very often produce a positive picture after a considerable exposure ; but as in these cases the picture has generally been first negative, and has afterwards, by a continuance of the chemical action, become positive, colouration is not often produced, although it is sometimes produced to a remarkable degree.

“ Daguerre noticed early in his experiments that red was sometimes reproduced in his pictures (on the iodised plate), and many artists have noticed the same fact, not only with regard to red, but to other colours.

“ I have experimented somewhat in iodine, bromine, fluorine, and their compounds, and regard the fluo-bromide of silver as giving the fairest prospect of success ; but as these substances will hereafter be treated of, both by themselves, and with regard to the power they have of accelerating M. Niepce's process, it would be out of place to mention them here. The isomorphism of iodine, bromine, chlorine, and fluorine, and the extraordinary parallelism of properties in the compounds of bromine and chlorine, are

points which no intelligent experimenter will overlook, and which may lead to important results. That colouration may be produced by means of iodine, bromine, fluorine, and their compounds, has been abundantly proved; and the person who first clearly shews why the iodised or bromidised plate sometimes takes a correct impression of the prismatic spectrum, while ordinarily negative pictures are impressed on it by light, will have made an exceedingly important contribution to photographic science. The process discovered by M. Natterer, of Vienna, for producing positive pictures on the iodised plate by the agency of the chloride of sulphur, does not help us along in this investigation as much as we might at first suppose.

“Iodine and sulphur can hardly be said to form a true chemical compound, and in the process above referred to, a sulphuret of silver is probably formed on the plate as soon as the decomposition of the iodide of silver is produced by light; and when, as in the ordinary iodised negative pictures, the lights are best produced, the sulphuret is formed with the greatest energy, and the deepest browns or blacks are produced. Hence the pictures become positive through a double decomposition of the iodide of silver and chloride of sulphur—a process somewhat analogous to the development of the mercurialised image. Having probably consumed sufficient space in considering the probability of success by other agents, it may be profitable to return to M. Niepce’s process.

“To render the process available, we must endeavour to render the plate more sensitive; and from some experiments, I am inclined to think it may be done in a manner somewhat analogous to the method by which Mr Talbot rendered the chloride of silver so sensitive in the calotype process; but from want of time, and being unfavourable for experimenting, I cannot speak certainly on the subject. By some late experiments with the hydrosulphuret of ammonia, I have been enabled to fix pictures which have not as



yet faded, though constantly exposed to ordinary light. The pictures fixed by it are much more permanent than those fixed by ammonia, as M. Niepce suggests; but the background of the picture is not quite so good. Chemistry presents us a large number of compounds, by some of which we may reasonably hope to accelerate and fix the picture. The carbo-hydrogens, ethers, fulminates, and cyanogen compounds, afford a large field for investigation. Those not well versed in the subject would do well to consult carefully Cane, Graham, Turner, or the large edition of Silliman.

“JAS. CAMPBELL.”

“The proper preparation of the chloridated plate, to enable it to receive coloured impressions, is an object of the first importance to those wishing to experiment on it, and consequently requires particular notice.

“The plate may be prepared by making it the positive pole of a battery, and letting it at the same time be immersed in chlorine water. The negative pole should be a slip of platinum. All the colours may be produced from a plate so prepared, if the chlorine and water are in the right proportions; but generally one colour or the other predominates according to the amount of chlorine in the liquid. By adding the chlorides of strontium, uranium, potassium, sodium, iron, or copper, to the liquid, various effects may be produced, and these bodies will be found to produce the same colour on the plate that their flame gives to alcohol. The honour of this discovery is due to M. Niepce. Copper gives a variegated flame; hence many colours may be impressed on a plate prepared with a solution of its chloride. M. Niepce recommends a solution of the mixed chlorides of copper and iron, and it is with these I have been most successful. As the chlorides of copper and iron are not much used in the arts, they are not generally found for sale in the shops; and it may be well to furnish those not much versed in chemistry with an easy

method of preparing them. They may be made directly from either metal, by dissolving it in hydrochloric acid; but they may be formed by a cheaper method, and by which also the acid fumes are avoided.

"Sulphate of iron or copper, or both together, may be dissolved in water, and then neutralized with common crude potass, or its carbonate or bicarbonate, known commonly as pearl-ash and saleratus. If either of the latter be used, then will be formed sulphate of potass, and a carbonate of the metal used, and there will also be a considerable effervescence of carbonic acid, which will, if care is not taken, cause the mixture to run over the vessel. After the copper or iron salt is neutralized, which is known by its ceasing to effervesce, the carbonate of the metal will settle slowly, and will at first nearly fill the vessel. The supernatant fluid, which is sulphate of potass in solution, may now be carefully poured off, and its place filled with water; this operation should be repeated several times, until the water which passes off is tasteless. The carbonate of the metal rapidly changes to an oxide by contact with the air, and it will generally be found, when it is sufficiently washed, that it is at least half oxide. On adding hydrochloric acid cautiously to the mixture, a chloride of the metal will be formed, and carbonic acid will be evolved from the remaining carbonate. The chloride formed is soluble; but as there are two chlorides of these metals, and we wish to produce the one which contains the most chlorine, it is best to add the acid cautiously, until the solution is decidedly acid.

"After filtering, the solution is fit for use; and it should be preserved in well-stoppered bottles. The water used should be rain or distilled water.

"About one part of the mixed chlorides should be used to three or four of water. The battery may be either Smee's, Daniel's, or Grove's; if of either of the former, it should be of two series; if of the latter, one cup is sufficient. The

plate, on being immersed in the liquid, almost instantly takes a violet colour. It should be allowed to remain from two to five minutes, according to the strength of the battery, and until it becomes nearly black. It should now be carefully washed, and afterwards heated over a spirit lamp until it takes a cherry-red colour, and it is then ready for exposure in the camera.

“Before speaking of exposing the plate, it may be well to speak of some difficulties which the inexperienced operator may find in preparing it. If the battery is not in good order, and a sufficient current is not passed through the solution, the plate will become coated, and apparently almost as well as when the battery is working well ; but on exposure it will give a negative picture, and but little coloured ; while if the battery is in good order, the impression is invariably positive. Sometimes on heating the plate after washing, the surface is covered with spots, or assumes a variegated appearance.

“This indicates that the solution is impure, or that the plates have not been thoroughly washed, and are still contaminated with the soluble chlorides which are contained in the solution.

“From the fact that the plate, if prepared with positive electricity, gives a positive picture, while, if prepared otherwise, it gives a negative ; it is evident that electricity plays an important part in the process. The same is true to some extent with the compounds formed with iodine, bromine, and fluorine. On heating the plate, the brown coating of chloride melts into a translucent enamel, and the heat should be withdrawn when a cherry-red colour is produced. If the heat is continued longer, the plate assumes a brighter colour, and becomes less sensitive ; and the enamel will finally scale off. To produce a picture by the ordinary process of M. Niepce, unaccelerated, it should be exposed for from three to five hours to sun-light in the camera, though pictures may be procured by contact in



from fifteen to thirty minutes. I will speak of accelerating the process hereafter.

“JAS. CAMPBELL.

“For the production of the best impressions by M. Niepce's process unaccelerated, an exposure of from three to five hours in bright sun-light is necessary; sometimes, when the enamel is very thin, a less time brings out the picture; but it is not so good, and the colours are not so brilliant. The picture with all its colours can often be plainly discerned under the enamel at the end of one hour or less, but it wants distinctness. The enamelled coating may be too thick, and in this case the exposure must be proportionately increased. For the production of the best effects, however, the enamel must be pretty thick, and the more translucent it is the better, as the light can better penetrate it. Pictures are obtained from varnished paper by contact in half an hour, on exposure to sun-light; but those taken in the camera are preferable, as they are more correct representations of the objects copied. I have found the observations of photographers as to the prevalence of the active or chemical rays during different periods of the day correct, viz. that the light is more active from 10 A.M. to 2 P.M., and that it is more active in the morning than in the afternoon. This I supposed to be a settled fact years since, but I see it occasionally announced as a new discovery. As to the fixing of the image permanently, I must confess my inability to do so, but will give the results of some experiments which may be instructive to others. If to freshly precipitated chloride of silver strong sulphuric acid be added, no new combination is formed, but the chloride is not afterwards altered by light. The acid in this case probably destroys the organic matter combined with the chloride, as scientific men generally agree in thinking, that when a salt of silver is decomposed by light, some organic matter, exclusive of the water of solution, must come into play. I have not, however, been able to fix the pic-

ture by this acid, as although it protects the unreduced chloride against the farther influence of light, it at the same time destroys the picture which is formed on the nearly reduced chloride under the enamel.

“M. Niepce suggests ammonia as a fixing agent. A small piece of Canton flannel, such as is used in cleaning the plate, may be moistened with aqua ammonia, and passed gently over the plate. If the plate is now allowed to dry, the ammonia evaporates, and the picture becomes more distinct. A better way is to expose the plate to the vapour arising from liquid ammonia.

“If the dry ammoniacal gas formed by heating sal ammoniac and lime in a retort be used, the picture will be covered with spots and spoiled.

“A picture fixed by means of this gas will not stand an exposure of more than two or three hours in ordinary light, and not one half hour in sun-light; yet it is much more permanent than one which has not been thus treated. Great care should be used in applying ammonia, or it will take off the enamel. Chloride of silver is soluble in ammonia; but when the volatile alkali evaporates, the chloride is left unchanged, except that it is not so sensitive to light.

“This probably arises from a partial destruction of the organic matter with which it is contaminated.

“The most effectual agent I have yet used is the hydrosulphuret of ammonia. One day, while endeavouring to fix a rather indistinct impression with aqua ammonia, it occurred to me to try the effect of the hydrosulphuret, which I had previously prepared to try as a fixing agent, but which I had forgotten to use.

“On the application of the hydrosulphuret very sparingly, in the same manner in which I applied the liquid ammonia, I could not perceive any great difference in the appearance of the picture, except that the background was tinged slightly yellowish, from the deposition of sulphur. Concluding that the picture was not sufficiently distinct to be kept as a

specimen, I poured on some strong liquid ammonia to take off the enamel, when, to my surprise, it took off the enamel, but left the picture below as strongly developed, and as distinct in outline, as the best daguerreotypes. I instantly poured on water to save the picture, and after contemplating it for some time, touched it, and spoiled a part of it. When it became dry, the enamel became hard again. I tried two other pictures, but always lost a part of the picture while endeavouring to take off the enamel. Having covered these pictures with varnish, and left them exposed to ordinary light, they lasted about ten days, and finally faded out. I am not sure but that they would have done better without the varnish, and intend to experiment farther on this agent. I have also tried rendering the plate electro-negative, and various other methods, which, as they have not been attended with success, it is unnecessary to recapitulate.

“JAS. CAMPBELL.”

“Having already treated at some length the proper preparation of the plate, for producing coloured impressions, the next thing in order is their acceleration and fixation. As I have not been able yet to fix the impression permanently, I have at present nothing more to say on the subject than was mentioned in my last communication.

“I hope, however, at no distant day to be able to speak positively in relation to this important part of the process; as acceleration of the process has already been produced to a considerable extent, it may be profitable to speak of it at some length.

“Much remains to be done to accelerate the process to the time in which ordinary daguerreotypes are taken; and the person who does so accelerate it will be second only to him who first permanently fixes the impression. Before speaking of any particular process of acceleration, I will advance a little theory on the subject, which is, I believe, founded on experiment and fact; but as I do not consider myself



infallible, I shall be obliged to any one who will shew, by well directed experiment, or new discovery, that I am in error. When coloured impressions are produced on the chloridated plate, the process seems to be merely the elimination of chlorine mixed with a little hydrochloric acid from the enamel, the acid being formed by the combination of the chlorine with the hydrogen contained in the organic matter or water mechanically mixed with the chloride. I am unable to say whether any portion of the chlorine eliminated re-combines with the silver under the enamel, but I think it does not. Hence I think, that we may safely predict, before experimenting, the substances which will be likely to act as accelerators. My theory on this subject is this: Those substances which rapidly reduce the chloride, and do not form new combinations with the silver or the remaining sub-chloride, will accelerate the process; also those which, by reducing the chloride, and continuing with the remaining sub-chloride or metallic silver, produce compounds which are susceptible of colouration. Many of the first mentioned substances, and some of the second class, seem to act as partial developing agents.

“ These substances may be divided into three classes. The first are those which combine with chlorine, under the influence of ordinary light, and which produce on the plate what chemists call single decomposition; that is, they abstract chlorine from the enamel, but leave uncontaminated sub-chlorine or metallic silver behind. Of this kind are hydrogen, sulphurous acid, carbonic oxide, and some other substances, both liquid and gaseous.

“ Second, those which unite with chlorine without sunlight, or even ordinary light, but which do not produce double decomposition, and which leave the plate nearly in the same condition as the agents before mentioned. Some of these agents accelerate the process, if the plate is exposed to their action before being placed in the camera, by weakening the affinity between the sub-chloride and the other atoms

of chlorine, which together form the chloride, or between the chlorine and silver of which the enamel is composed, and thus render the plate more sensitive to light. They also act as at least partial developing agents. Of this kind are carburetted hydrogen, and some other substances.

"The third class comprises those substances generally, which weaken the affinity of the chlorine for the silver, but which become themselves mixed with the chloride, on account of their being isomorphous with it, or unite with the reduced silver by double decomposition. Of this kind are iodine, bromine, fluorine, chromic and chloro-chromic acids, cyanide and ferrocyanide of potassium, sulphuretted hydrogen, oxygen, and some other agents. There are some other substances, as aldelyzed ether, and some similar compounds whose action cannot be so satisfactorily accounted for, although promising much.

As an accelerator which we cannot reckon among chemicals, we may mention electricity. Its action is merely reducing the chloride, by eliminating chlorine from it. It acts in the same manner with iodine and bromine in the ordinary daguerreotype process; and as here the decomposition is only commenced, before the plate is taken out and exposed to mercurial vapour, the process is by it very much accelerated. The only secret in applying electricity is to render the plate positively excited while in the camera; and this may be done in a variety of ways. A good way is to make the plate a part of the conducting medium, as it then receives the whole force of the battery.

"The plate may also be excited by thermo-electricity, by connecting two long strips of copper and zinc with the plate in such a manner as to positively excite the plate, and heating the ends projecting out of the camera box, at the point of junction, by a spirit lamp. The plate may also itself form a part of the battery. Let a square of cotton flannel, such as is used in cleaning the plate, be soaked in a hot solution of salt or sulphate of soda, and then applied to the back of the

plate, and covered by a piece of platina or amalgamated zinc, according to the kind of electricity we wish to excite. One end of the last plate must project over the cotton, and touch the copper plate. On placing the cap over the plates, we have a miniature battery, which will answer the double purpose of exciting and heating the plate. On many days when daguerreotypes cannot well be taken, on account of a want of positive electricity in the air, these methods of exciting the plate may be used with great advantage by the daguerrean artist. I may have something more to say on electricity at some future time. "JAS. CAMPBELL."

*Hydrogen, No. 6.*

As hydrogen has been often mentioned in my attempts to explain the theory of Heliochromy, and as it seems to play an important part in most decompositions caused by active influence, it requires more than a passing notice. I do not, however, intend to enter into all the details connected with its history and preparation. These are familiar to all even moderately versed in science, and those not versed in chemistry can inform themselves fully on the properties of hydrogen, by consulting any respectable work on chemical science.

"Hydrogen is a powerful electro-positive body ; hence it combines with electro-negative bodies, such as oxygen, fluorine, chlorine, iodine, and bromine, with great energy. The metals are generally powerfully electro-positive bodies ; hence they form no combinations with hydrogen, but generally unite readily with chlorine, iodine, and the bodies mentioned in connection with them. These compounds of the metals with the bodies above mentioned seem to be uninfluenced by light, unless they are contaminated with organic matter or water, and in the latter case most probably from organic matter contained in the water. Hydrogen is also the most powerful reducing agent known in chemistry, and it acts almost equally well in reducing all



metallic compounds, oxides, sulphurets, carburets, &c. to the metallic form. To reduce these rapidly, the hydrogen must be in its nascent form.

“Chloride of silver is rapidly reduced by nascent hydrogen; but when the hydrogen is generated at some distance from it, it requires a long time for its reduction. This reduction is assisted by light, especially sun-light which abounds in the actinic rays; hence it is a very powerful accelerator in producing impressions on the chloridated plate.

“It is also, according to theory, a very proper agent for accelerating this process, since it forms no compound with the reduced or partially reduced chloride, and the results of its action are similar to those of light, or more properly actinism. I have mentioned in a former article the active combination of chlorine and hydrogen in sunlight; also by means of electricity and spongy platinum, and their slower combination by ordinary light, and by means of a plate of clean platinum; it will therefore be unnecessary to recapitulate them at present. If the chloridated plate be exposed to hydrogen, while in the camera, the process will be much accelerated, and the colours lose none of their brilliancy; in fact, in some cases they are more brilliant than they would be otherwise.

“The action in the camera seems to be this: the hydrogen, under the influence of light, has a powerful tendency to withdraw chlorine from its combinations, and a small portion of hydrochloric acid is formed.

“This latter substance is diffused among the remaining hydrogen, or escapes with it through the box, which can hardly be made tight enough to confine it.

“The decomposition of the chloride by the hydrogen, is in proportion to the colours of the image on the plate, the different coloured rays of the spectrum having different actinic power; hence the results of the action of hydrogen and actinism are very analogous. If the opinion of the most

distinguished philosophers is true, namely, that there can be no actinic decomposition unless there is an elimination of free hydrogen, it will be seen that we are only assisting nature by applying hydrogen to the plate.

"There are some difficulties in the application of hydrogen, the principal of which is its excessive lightness, it being nearly fifteen times lighter than air, and it escapes from the box nearly as soon as it is generated ; and were it not for the property of gases to diffuse themselves in air, but little of the hydrogen would reach the plate. The box should be made as tight as possible, and the hydrogen should be generated either in a vial in the camera box, or in a bottle out of the box. In the latter case, the gas may be conveyed in an india-rubber tube through the screw hole in the bottom of the box. The latter method is the best, as more gas can be produced by using a larger generating vessel.

"I have intended to try the minimum time in which a picture can be produced by the aid of this gas. I proposed to place the object to be copied on the ground, and place the camera vertically over it. The gas would then be constantly in contact with the plate, and the maximum action would be produced. I have not been able, owing to the multiplicity of other engagements, to satisfy myself on this point as yet. The process is by the other method fully accelerated two-thirds. I will mention another difficulty in preparing plates, which can sometimes be remedied by this gas, and would be likely to cause a great deal of trouble and perplexity to beginners. If the chloridated plate be prepared according to the directions previously given, with fresh solutions, the results will always be satisfactory.

"JS. CAMPBELL."

*"Sulphur.*

"Although sulphur is not of itself of any great importance in photography, yet some of its compounds are possessed

of great photographic sensibility, and deserve more than a passing notice. Any one at all conversant with chemistry is aware of the great rapidity with which the black sulphurets of silver are formed by the action of the sulphuretted hydrogen on the salts of these metals.

“Chemists have not as yet determined whether this action is dependent in any degree on light. Several processes have been lately discovered by which photographic images may be formed on silver or glass plates by the decomposition by light of the iodide or chloro-iodide of sulphur. These processes were discovered by Messrs Natterer, Pucker, and others. Mr Pucker uses mercury in connection with iodine and sulphur; but Mr Natterer does away entirely with mercury in his process. According to Mr Hunt, sulphur is often an indirect agent in the calotype processes, as much of the paper used is bleached with sulphurous acid, instead of chlorine, and is consequently contaminated with traces of sulphur. Sulphur does not directly have much effect on the chloridated plate. I have rubbed the plate with it before exposure, and apparently without either advantage or detriment to the image. Sulphurous acid, on the contrary, acts as an accelerator by combining with the chlorine of the chloride, and reducing the thickening of the enamel. It is most conveniently used in the liquid form. I have been more successful in my attempts to fix the heliochromic image with the compounds of sulphur, than with any other substances; but the pictures have in each case lost somewhat of their tone and brilliancy of colour.

“I have used sulphuric acid, sulphuret of carbon, chloride of sulphur, and hydrosulphuret of ammonia.

“No very interesting results followed from the application of the acid, or the sulphuret of carbon, and I have before mentioned that the hydrosulphuret of ammonia was valuable as a fixing agent; but by exposing plates alternately to the latter agent, and to chloride of sulphur, I succeeded in



fixing impressions so that they withstood strong light four weeks before fading out. This encourages me to believe that heliochromic pictures can, ere long, be exhibited by the side of, and equally permanent with, daguerreotypes.

*“ Chrome.*

“ This metal, it is well known, derives its name from the variety and brilliancy of the colours of its compounds.

“ It was hence much experimented on by photographers in the early stages of the photographic science, but was, from the singular permanence of its compounds under the action of light, given up by most of them as an unprofitable subject for experiment.

“ Later, however, the experiments of Mungo Ponton, Becquerel, and others, have proved it to possess a considerable degree of photographic sensibility; and still later the experiments of Hunt and Talbot have given to this substance a new interest.

“ Having been of late unavoidably interrupted in my experiments, I cannot say as much on this substance as I could wish, but I will give the results of some experiments with it which may prove interesting to your readers. The compounds of this metal which I have used most, are the chlorochromic acid, and the perfluoride of chrome.

“ The first may be easily prepared by placing one part of common salt, and a little more than one and a half parts of bichromate of potash in a porcelain cup, and after well mixing the materials, pouring on them four parts of strong oil of vitriol. A deep red vapour is instantly given off, which resembles bromine vapour very much in appearance and odour. This may be condensed, and is then a blood-red liquid, which gives off red vapours when exposed to the air. This gas is, however, so easily produced, that it is unnecessary to keep it in a liquid form.

“ The perfluoride of chrome is produced in the same manner by substituting powdered fluor-spar for the common

salt in the last process. It is of a fine dark red colour, and cannot be liquified by pressure at ordinary temperatures. If the chloridated plate be exposed for an instant to either of these gases, it takes a deeper red colour; and if exposed too long, it takes a purple colour, which shews that some of the chromate of silver has been formed on its surface. This is unfavourable, for if the chromate is formed, it loses its sensibility. The proper point seems to be, that where the affinity of the chlorine for the silver is disturbed and not destroyed, and the colour and translucency of the enamel is not much affected. At this point the process is accelerated, and the impression is rather more stable than on the simple chloride.

“I have experimented considerably on the compounds of chrome, with iodine and bromine, and also on the mercurialised plate, and have produced some singular results, but have not experimented sufficiently to satisfy myself fully on the subject. At some future time I may have some more to say of it. The chromate of silver is not described in the ordinary works on chemistry. It is of a deep purple colour, and not easily affected by light, unless combined with other substances, or acted on at the same time by other agents than light. The chromates of iodine and bromine are reduced more easily, and generally give negative pictures. I say chromates of iodine and bromine for convenience, for the compounds which they form are analogous to those which chrome forms with chlorine and fluorine, and are not true chromates, but rather iodochromic acids, &c. These compounds promise considerable, and present a wide field for, experiment.

#### “*Fluorine.*”

“This element is most frequently found in the mineral kingdoms, in combination with calcium, forming fluor-spar. It appears to possess more powerful genial affinities than any other elementary body, and is therefore the most diffi-

cult to isolate and examine. On this account but little is known of it, although the best chemists have devoted much time to its examination. \* \* \* Of late, fluorine has been found to be an important substance in photography. Several instantaneous processes, (in which it plays an important part), have been discovered by the French photographers, and one by Mr Talbot. Professor Hunt, however, was the first to use fluorine (in photography), and his process, designated the Fluorotype, is an elegant one, equally valuable for its simplicity and certainty. He also was the first to produce a coloured spectrum on the fluoride of silver, and was very sanguine as to its ultimate production of coloured photographs by its use. Professor Hunt has demonstrated that a coloured spectrum can be produced with equal certainty on the fluoride, as on the chloride of silver spread on paper. It is probable that the fluoride of silver on the metal plate will copy coloured lithographs.

“ The chloridated plate must be treated with aqueous chloride, and it is best prepared by the galvanic battery. The plate cannot be thus prepared with fluorine, for it will be found that if the silver plate be rendered electro-positive in a solution of some fluoride, that the fluoride of silver being soluble, is dissolved from the plate as fast as it is produced on the surface by the battery. Again, if we expose the silver plate to dry chlorine, it will be covered with a white coating of chloride of silver, which gives a negative picture on being exposed to light; and I have proved that if the silver plate be exposed to fluorine, it is affected similarly by light, but much quicker. If a mixture of powdered fluor-spar and black oxide of manganese be treated in a retort with sulphuric acid, an impure fluorine is liberated. \* \* \* If the silver plate is exposed to this gas, it soon becomes covered with a white or greyish white coating, which is impressed by light with great rapidity, and gives a negative image similar to the chloride. Hence we see that there is a great parallelism between



the photographic properties of chlorine and fluorine. \* \* \* I stated that there are many difficulties in preparing the silver plate with fluorine by electricity, but I hope to shew at some future time, that they are not insurmountable. The plate prepared from the impure fluorine, generated by the action of sulphuric acid, as fluor-spar, and the black oxide of manganese, is contaminated with the per-fluoride of manganese; and the experiments performed with it are, although striking, not at all conclusive as to the capability of colouration of the fluoride of silver. I will now, for the satisfaction of those fond of experimenting, give some of my results from experiments on the chloridated silver plate with hydro-fluoric acid, and the soluble fluorides.

“If a plate prepared to receive coloured impressions be exposed to the fumes of hydro-fluoric acid, it takes a deeper red, and is acted on quicker by light, and the reds of the picture are the strongest. The results are better if the acid is mixed with the chlorides of copper and iron, with which the chloridated plate is best prepared.

“The plate is then in fact prepared with a fluo-chloride of silver, and is much more sensitive to the light than the simple chloride. I prefer, however, the fluorides of potassium or sodium, to hydro-fluoric acid, for admixture with the solution of the chlorides above mentioned, both because they do not require so much care in manipulating, and because they give better results. These fluorides are both very soluble, and are easily prepared by neutralizing soda or potass, or their carbonates, with hydro-fluoric acid

\* \* \* The process described by Professor Hunt, under the name of the Fluorotype, is worthy the attention of all experimenters on paper. Portraits can be taken with it, and the process is free to all (see Hunt's Photography). I have not been able to produce a coloured spectrum on this paper, although Professor Hunt has done so. A sheet of waxed paper, soaked several hours in a solution of fluoride of sodium, and then washed with the silver solution, takes

a good impression. If one of these papers be exposed to sun-light, and allowed to darken, it darkens unevenly, and shews a variety of colours, brick-red being the predominant one. A paper prepared with the pure fluoride of silver would undoubtedly be better, and I intend to try it soon.

"I have noticed that the presence of the nitrates in any form is always fatal to the production of colours.

"J. CAMPBELL."

*"Iodine."*

"The history and general properties of this substance are so intimately connected with the history and practice of Heliographic science, that it may seem to many that nothing new can be said on it, and that its action, under the influence of light, is fully understood.

"Yet, although it has the foundation of almost all photographic processes, ever since the daguerreotype and calotype were discovered, it may be possible that we do not fully understand its properties. I will take the liberty of making a few suggestions as to the probability or possibility of producing coloured impressions on iodine, which my readers can take for what they are worth; and I am induced to do this from the fact, that daguerreotype operators are generally better acquainted with the properties of this substance than with chlorine and fluorine.

"It seems to be the universal opinion, that colouration cannot be produced on the iodised plate; yet every work on photography mentions the occasional production of coloured spectrums; and some rare cases are mentioned where one single colour, generally red, has been produced on the mercurialised impression. I have myself seen a drab-coloured brick house with green shutters, taken by Bisbee, of this city, well represented on the plate. The prevailing colour was correctly given, and the shutters were of a reddish brown.

"Scientific men and artists have not as yet been able to

assign a cause for these occasional specimens of colouration, nor are they able to produce them at will. I will venture a few suggestions on this subject, which will, I hope, induce others to examine it more closely than I have at present leisure to do. I think the production of either positive or negative impressions, at the pleasure of the operator, on the same chloridated plate, affords some clue to the negative impression produced on the iodised plate, or at least by analogy, gives us some data to start upon, in investigating this subject. In the course of almost numberless experiments on the chloridated plate, I found that whenever the enamel contained oxide of silver, the invariable result was a negative impression. The contamination with oxygen was generally produced by the solution from which the plate was prepared having absorbed it, in which case it passed over to the positive pole in company with the chlorine, or by the decomposition of some accelerating substance placed on the plate, while subjected to the action of the light in the camera. In the latter case, substances which, on decomposition, furnished hydrogen or carbon, or both in conjunction, produced positive impressions, while those which yielded oxygen produced negatives. Some of the former class were chloride of olefiant gas or Dutch liquid, spirits of turpentine, most essential oils, composed of carbon and hydrogen, and even some of the fatty oils. Some of the latter class were the vapours of nitric and acetic acids, most essential oils, containing oxygen and many other substances. The chloride of olefiant gas acts by abstracting chlorine from the enamel—and furnishing hydrogen at the same time, and it is the best liquid accelerator I have tried. The generally received opinion as to the condition of the silver on iodated paper and iodised plates, after being exposed to the action of light, is, that on the paper it is in the form of oxide, and that it becomes an iodurate on the plate. Some



chemists—Kane and others—however, think that the reduced silver on the plate also becomes an oxide.

“ Now, not wishing to decide where doctors disagree, I will merely suggest that the silver may, if principally ioduret, be contaminated with oxygen to such an extent as to render colouration impossible. Every one, at all conversant with chemistry, knows how readily iodine combines with oxygen. Silver has also the curious property of combining with oxygen when hot, and parting entirely with it as it cools. Thus a mass of molten silver will absorb much oxygen, and may even absorb twenty times its volume. This oxygen it appears to hold rather dissolved than combined, for, as the metal cools, the gas is entirely eliminated, and its surface thereby thrown into irregular granulations.

“ This may, together with electric excitation, be the cause of the beneficial effect of buffing the plate before exposing it to iodine, as the temperature is thereby considerably raised. Some of the best operators I have ever known are in the habit of heating their plates in cold weather while exposed in the camera, and with good effect. It seems to me then that we have some clue to the usual insensibility to colouration of iodine. May not the reason why coloured spectrums are never impressed on simple iodated papers, and their occasional production on the iodised plate, be partly owing to the fact that, in the former case the reduced silver always takes the form of oxide, while in the latter it may sometimes be free from it? With these suggestions I will close at present, and in my next will give the results of some experiments with iodine and its compounds.

“ JS. CAMPBELL.”

“ My first experiments were on the chloridated plate, prepared to receive coloured impressions. I found that when the plate so prepared was exposed to the vapour of iodine (about a minute) in the coating box, the colour of the ena-

mel was deepened, and the impression was obtained in less time than on exposure in the camera.

“The impression was generally positive, but the colours were not as good as would have been produced on the plate if it had not been exposed to the iodine vapour. The impression was also more fugitive than on the simple chloridated plate, and I have not been able to fix it. The chloride and fluoride of iodine gave much better results, but of the same general character. In each case, if the plate had been too long exposed to the vapour, negatives, nearly or wholly devoid of colour, were produced. Knowing that the presence of water was essential to the production of colour on the chloridated plate, I exposed the plate to the vapours of iodine in solution, but the results were nearly the same. I then exposed the iodised plate, prepared by the battery from a solution of copper in iodide of potassium, in the camera, and found it gave negatives with apparently no trace of colouration. After many experiments, finding some of the compounds of chrome useful accelerators on the chloridated plate, I concluded to try them on the iodised plate. The iodised plate was either exposed to the vapour of chloro-chromic acid, or to simple chromic acid. The latter combination was effected by immersing the plate for a short time in a solution of bichromate of potass, or, better, by making the plate the positive pole of a battery in the same solution, when one equivalent of chromic acid, combined with the iodide of silver and neutral chromate of potash, passed to the negative pole. The plates so prepared usually lost some of their sensibility, and if combined with too much acid, become almost wholly insensible to light. The impressions were mostly negative and devoid of colouration, but some of them shewed decided traces of colour. Some of the plates were exposed a short time in the camera, and afterwards exposed to mercury, but generally produced negatives, though on some of them the yellow chromate of mercury and red chromate

of silver could be seen, but not always in the proper place. I am inclined to think these cases to be the result of chemical affinities not altogether, if at all, influenced by the coloured rays. Some of the specimens were exposed in the camera, and subjected to mercurial vapour at the same time. The results, however, were nearly the same. Some of the iodised plates, combined with chrome, were exposed to mercury before being placed in the camera, and though apparently insensible, yet, after some hours' exposure, eventually developed an image, which was in some cases positive, and shewed some colouration, but generally negative. I have found that, contrary to the opinion expressed in photographic works, the iodised plate is capable of developing an image, if exposed to mercury before being placed in the camera, but the light must be strong, and the exposure protracted, and that the impression is generally negative.

“ I should also state that I have used coloured glass in some of these experiments, but with no very striking results. The above experiments are certainly encouraging, and I give my imperfect results to others, in the hope that some one may perfect them. “ J. CAMPBELL.”

In October 1853 a correspondent of Humphrey's Journal, New York, writes :—“ I have noticed with some astonishment, that our scientific operators have never broken loose from the idea, that nothing but the salts of silver, in some form or other, can be rendered sensitive to the operations of light. Noticing this some two years ago, I commenced some experiments with other substances. I have endeavoured to make a substance analogous to the substance of the flowers of the field ; one reflects one ray of light, another another, and so on throughout the botanical kingdom. I have used Chinese rice paper, prepared in such a manner that it is nearly transparent ; and the actinic,



chemical, and all other rays of light, pass through the substance, leaving their own peculiar hue,—whatever ray of light, in whatever degree of combination of colour striking the substance, stains it so completely, that both sides are completely coloured like stained glass. So long as it is kept in a feeble or subdued light, it is as deep as nature itself; but upon bringing it to the light of day, it passes away like the breath upon a mirror. I am in hopes of eventually succeeding in fastening them permanently. If so, you shall have my process in full to publish to the world. I am perfectly satisfied that we are only on the threshold of nature's laws and operations, and that there is a vast field open for investigation. There need be no jealousy, for there is enough for all to do."

A paragraph has appeared in the newspapers, stating that a Swede, M. Carloman,<sup>1</sup> has invented a new process of printing, which he calls Photochro-mography, by which he obtains prints of objects in their natural colours by the aid of light. We have seen no account of the process, but it seems probably only an application of the ordinary methods of colour-printing, as executed by lithographers, to engravings on stone or zinc, obtained by the processes of M. Martin or MM. Barreswil and Lemercier.

NEW RESEARCHES ON THE COLOURED IMPRESSIONS  
PRODUCED BY THE CHEMICAL ACTION OF LIGHT.  
BY M. C. BECQUEREL.

*(From the Comtes Rendus.)*

"The chemical action of light, as is well known, has enabled me to render evident the electrical effect produced through the reactions which take place under the influence of luminous radiation. On the other hand, I was led more than six years ago to observation on the fact, that it is possible to prepare a surface chemically impressionable by light, in such a manner that it will be coloured precisely

with the tint of the luminous rays impinging on it. The sensitive substance which possesses this remarkable property is a chloride of silver, which may be called the violet chloride, containing less chlorine than the white chloride, and presenting itself, in general, mixed with the latter. The chloride of silver in question is susceptible of being placed in such conditions, as to be only affected between the limits of refrangibility of the rays perceptible to the organ of vision. It was important to study attentively the manner in which it would behave in the apparatus which I have called an electro-chemical achrometer, the effects resulting from the action of the different luminous rays, the intensity of which should be varied within determinate limits ; and lastly, if it were possible to establish a photometric method founded upon principles different from those ordinarily in use. In a former memoir (*Ann. de Chimie et de Physique*, xxxii. 176), I had already commenced this study ; but I was led to recognize the necessity of examining anew the different circumstances which accompany the preparation of the sensitive substance, and the modifications produced by heat and light before the luminous rays impress their colour upon it. Such is the aim of the work I now have the honour of submitting to the Academy.

“In preceding publications I have made known various means, by the aid of which one might obtain surfaces coated with the violet chloride of silver giving coloured impressions ; but that which gives the best effects consists in decomposing rapidly, by an electric current, a solution of hydrochloric acid in water, and bringing the chlorine upon a plate of silver placed at the positive pole of the pile. The process is rendered of certain and easy application by determining, in each circumstance and at each instant, the quantity of chlorine conveyed to the plate of silver. For this purpose a water voltameter is interposed in the voltaic current, so that the current which decomposes

the hydrochloric acid, and carries the chlorine to the silver, equally decomposes the acidulated water; the electro-chemical decompositions only taking place in definite proportions, a quantity of chlorine is carried to the plate of silver, equal in volume to the hydrogen gas set free in the tube placed above the negative electrode of the voltameter. The back of the plate of silver is protected by a varnish, so that the chloride shall only be carried to one surface.

"The memoir contains all the indications relative to the different circumstances of the preparation of the impressionable plates, which circumstances must not be neglected.

"It was found that it was most advantageous to operate so that the quantity of chlorine carried to the silver plate lay between the limits of 4 and 7 cubic centimetres of chlorine, at ordinary temperatures, to every square decimetre of silver surface. Within these conditions, the thinner the film, the more impressionable is the substance, but the less beautiful are the gradations obtained.<sup>1</sup> With a thicker coat than the above, the results were not so satisfactory.

"If we project a luminous spectrum upon an impressionable surface thus prepared, we obtain before long an impression which commences in the yellow and orange, that is to say, in the most luminous portions of the prismatic image, and extends as far as the red and violet extremities. This impression, as I have already demonstrated in a preceding memoir, reproduces the different coloured tints of the spectrum. But the tints, although very vivid, are rather dark; and on the red side, between the lines B and A, and beyond A, the impression turns violet, and blackens rapidly. When the preparation has been made according to the directions given in the essay, no impression is seen beyond the violet; and except the black colouration on the red side, the image does not extend much beyond the limits A and H, and occupies the same extent as the visible

<sup>1</sup> This same fact also applies to the ordinary daguerreotype process.



spectrum. If mixed luminous rays impinge upon the sensitive surface, they leave, like the rays of the spectrum, a coloured impression of the same tint as they possess themselves. But this same substance, when submitted to the influence of heat or light before the action of the luminous rays, conducts to remarkable results, which must next be discussed.

“ The action of heat profoundly modifies the violet chloride of silver. An elevation of temperature of  $212$  to  $320^{\circ}$  Fahr. causes the tint of the prepared plate to change, without causing it to lose traces of chlorine, but at the same time it changes the mode of action of the various luminous rays: diffused light, or direct solar light, acts as white, instead of giving an impression of a grey tint; and moreover, the coloured tints are light, instead of being sombre, as before the heating. But the remarkable point is, that by keeping the temperature between  $86^{\circ}$  and  $95^{\circ}$  F. for several days, the same end is obtained, and with far better results. The yellow and green tints, which in the action of the luminous spectrum upon a plate heated to a high temperature are not reproduced clearly, make their appearance under these conditions; adding to this, the sensitive substance is more rapidly impressionable. Thus plates prepared in this manner may be used for reproduction of the coloured images of the camera obscura. One cannot attribute to a chemical action the effect produced upon the chloride of silver by a difference of temperature so slight, although continued for several days.

“ Probably this circumstance involves a modification of the physical condition of the impressionable substance. It would then be an effect of the same kind as that which takes place in the formation of red phosphorus. The action exerted by the less refrangible rays of light is also very curious, for it leads to a result analogous to that which is obtained by prolonging the elevation of the temperature of the plates. It seems, therefore, that molecular effects of

the same order are produced in both cases. The luminous spectrum acts in the following manner upon chloride of silver, modified by the extreme red rays. The action commences as before, in the orange, the yellow, and the green; then extends little by little towards the violet and towards the red.

“All the tints corresponding to the colours of the spectrum are light, as if the plates had been heated; but the prismatic impression is far more beautiful, and even the green, yellow, and orange have more vivid tints than before the action of the extreme red rays. Thus the advantage possessed by the chloride, modified by the less refrangible rays, over that which has been heated, of giving a black ground upon which the different prismatic colours become depicted, is combined with that of perfectly preserving the green and yellow tints. On the red side the image of the spectrum only gives a brilliant tint as far as B; beyond this limit, the black colour which should be produced being that which prevails on the whole surface, no effect takes place at the first moment. But if originally the chloride has been kept only an insufficient time under the action of the extreme red rays, the solar spectrum still gives a deep impression beyond B and A.

“On the substance thus modified by heat or light, we may obtain very beautiful coloured reproductions of the luminous spectrum. The figures of coloured rings, and those given by crystallized plates traversed by polarized light, are equally well represented with their tints. Even the images of the camera obscura may be reproduced, painted, so to express, by light; but these reproductions, although having more vivid colours than those which I obtained some years ago, have at present only a scientific interest, and, for the present, we must not think of their practical application, since the impressions can only be preserved in the dark. I have not yet been able to arrest the subsequent action of diffused light, which gradually

destroys the images ; it is only in a transitory condition, so to speak, that the impressionable substance has the property of reproducing colours."

Mr Henderson, of Blackford, Edinburgh, has used a very easy method to produce the colours on the daguerreo type plate, and with a preparation to be procured at all times with facility, viz. to two ounces of water add four drops of hydrochloric acid and four drops of saturated common salt ; then filter the solution ; plunge the plate into this quickly after cleaning it well on the back, and allow it to remain about five minutes or so, when it will have a dark appearance on the silver surface ; after well washing in water, heat it with the lamp till it is red coloured. This plate copies all the colours of a drawing placed over it besides the white.

In the preceding pages, it has been the object of the compiler to include all the processes in Heliochromy which will be really useful to amateurs ; and after recommending them to a practical acquaintance with M. Becquerel and M. Niepce's processes, they will possibly be enabled to introduce much improvement, and thus realize the hope that painting by light will be brought to perfection.

As it is absolutely necessary that the plate should be well polished, the following method is given :—A fir board 24 inches by 16, may be covered with two plies of ironing blanket, and white velveteen over it ; put some olive oil and fine washed rotstone on one corner of the board to begin, on another corner put some fine rouge, and leave a third corner quite clean to finish. An old plate, after being rubbed on the rotstone and oil, and then cleaned off on another part of the board, is rubbed on the rouge, and finished on the clean part ; a new plate may be done on the rouge and the clean part at once. The board requires a paper or pasteboard cover to keep it quite free from dust when not in use.